

CLAIMS

What is claimed is:

1. A fluorine-containing copolymer comprising ;
 - (a.) a first repeat unit derived from an ethylenically unsaturated compound containing a functional group having the structure:

$$-X_r(\text{CH}_2)_q\text{C}(\text{R}_f)(\text{R}_f')\text{OH}$$
 wherein
 - R_f and R_f' are the same or different C_1 - C_{10} fluoroalkyl groups, or taken together are $(\text{CF}_2)_n$;
 - n is an integer from 2 to 10;
 - X is S, O, N, or P;
 - $q = 0$ and $r = 0$, or $q = 1$ and $r = 0$ or 1 ; and
 - (b.) a second repeat unit derived from an acrylate selected from the group consisting of $\text{CH}_2=\text{CRCO}_2\text{R}''$ and $\text{CH}_2=\text{C}(\text{CH}_2\text{OH})\text{CO}_2\text{R}'''$,
 wherein
 - R is H, F, or a C_1 - C_5 alkyl or fluoroalkyl group;
 - R'' is a polycyclic C_5 - C_{50} alkyl group containing at least one hydroxy group; and
 - R''' is a C_1 - C_{25} alkyl group.
2. The fluorine-containing copolymer of Claim 1, wherein (b) is tert-butyl hydroxymethylacrylate.
3. The fluorine-containing copolymer of Claim 1, wherein (b) is hydroxyadamantyl acrylate.
4. The fluorine-containing copolymer of Claim 3, wherein the polymer further comprises a repeat unit derived from 2-methyl-2-adamantyl acrylate.
5. The fluorine-containing copolymer of Claim 4 made by a semi-batch synthesis.
6. The fluorine-containing copolymer of Claim 1, further comprising a repeat unit derived from a fluoroolefin selected from the group of ethylenically unsaturated compounds containing at least one fluorine atom covalently attached to an ethylenically unsaturated carbon atom.
7. The fluorine-containing copolymer of Claim 6, wherein the fluoroolefin is selected from the group consisting of tetrafluoroethylene,

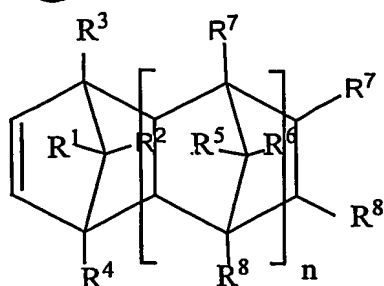
chlorotrifluoroethylene, hexafluoropropylene, trifluoroethylene, and $R_f\text{OCF}=\text{CF}_2$ wherein R_f is a saturated fluoroalkyl group of from 1 to 10 carbon atoms.

8. The fluorine-containing copolymer of Claim 1, wherein $r=0$ and $q=0$.
9. The fluorine-containing copolymer of Claim 1, wherein $q=1$ and $r=0$.
10. The fluorine-containing copolymer of Claim 1, wherein $q=1$ and $r=1$ and X is S, O, N or P.
11. The fluorine-containing copolymer of Claim 1, further comprising a repeat unit derived from at least one ethylenically unsaturated compound containing a functional group having the structure

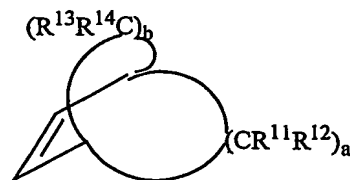


wherein R_f and R_f' are the same or different fluoroalkyl groups of from 1 to 10 carbon atoms or taken together are $(\text{CF}_2)_n$ wherein n is 2 to 10 and R_a is an acid- or base-labile protecting group.

12. The fluorine-containing copolymer of Claim 11, wherein R_a is $\text{CH}_2\text{OCH}_2\text{R}_{15}$, and R_{15} is hydrogen, a linear C_1 - C_{10} alkyl, or a branched C_3 - C_{10} alkyl group.
13. The fluorine-containing copolymer of Claim 1, wherein the functional group of repeat unit (a) is $-\text{C}(\text{CF}_3)_2\text{OH}$.
14. The fluorine-containing copolymer of Claim 6, wherein at least one repeat unit is cyclic or polycyclic.
15. The fluorine-containing copolymer of Claim 6, further comprising a repeat unit derived from a cyclic or polycyclic unsaturated compound, selected from the group of compounds represented by structures (H) or (I),



(H)



(I)

wherein:

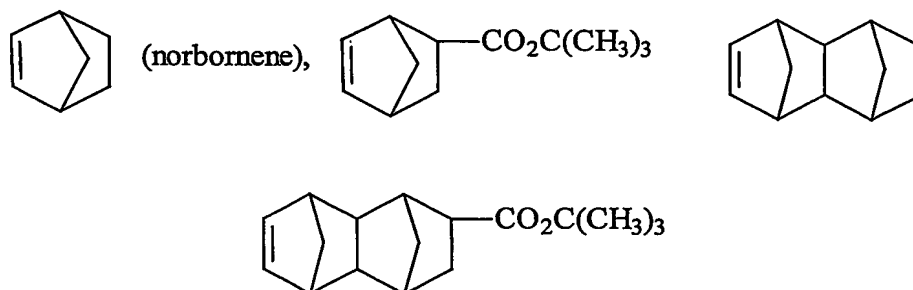
n is 0, 1 or 2;

a and b are independently 1, 2 or 3, except that a is not 1 when

b is 2 or vice versa; and

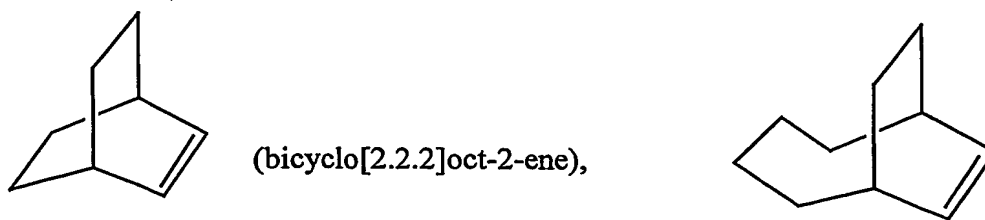
R^1 to R^8 and R^{11} to R^{14} are the same or different, and each represents a hydrogen atom, a halogen atom, a carboxyl group, a C_3 to C_{14} secondary or tertiary alkyl carboxylate, a hydrocarbon group or a substituted hydrocarbon group.

16. The fluorine-containing copolymer of Claim 15, wherein the cyclic or polycyclic unsaturated compound is selected from the group consisting of:



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16. The fluorine-containing copolymer of Claim 15, wherein the cyclic or polycyclic unsaturated compound is selected from the group consisting of:



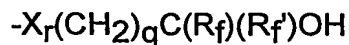
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18. The fluorine-containing copolymer of Claim 7, wherein the fluoroolefin is tetrafluoroethylene.

19. A photoresist comprising:

(a) a fluorine-containing copolymer comprising:

- 5 (i) a first repeat unit derived from an ethylenically unsaturated compound containing a functional group having the structure:



10 wherein

R_f and R_f' are the same or different C_1 - C_{10} fluoroalkyl groups, or taken together are $(\text{CF}_2)_n$;

n is an integer from 2 to 10;

X is S, O, N, or P;

15 $q = 0$ and $r = 0$, or $q = 1$ and $r = 0$ or 1; and

- (ii) a second repeat unit derived from an acrylate selected from the group consisting of $\text{CH}_2=\text{CRCO}_2\text{R}''$ and $\text{CH}_2=\text{C}(\text{CH}_2\text{OH})\text{CO}_2\text{R}'''$,

wherein

20 R is H, F, or a C_1 - C_5 alkyl or fluoroalkyl group;

R'' is a polycyclic C_5 - C_{50} alkyl group containing at least one hydroxy group; and

R''' is a C_1 - C_{25} alkyl group; and

(b) at least one photoactive component.

25 20. The photoresist of Claim 19, further comprising a dissolution inhibitor.

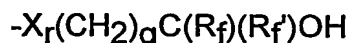
21. The photoresist of Claim 19, further comprising a solvent.

22. A process for preparing a photoresist image on a substrate comprising, in order:

- 30 (1) applying a coatable photoresist composition on a substrate, wherein the coatable photoresist composition comprises:

(a) a fluorine-containing copolymer comprising:

- 35 (i) a first repeat unit derived from an ethylenically unsaturated compound containing a functional group having the structure:



wherein

R_f and R_f' are the same or different C_1 - C_{10} fluoroalkyl groups, or taken together are $(CF_2)_n$;

n is an integer from 2 to 10;

X is S, O, N, or P;

5 $q = 0$ and $r = 0$, or $q = 1$ and $r = 0$ or 1 ; and

(ii) a second repeat unit derived from an acrylate selected from the group consisting of $CH_2=CRCO_2R''$ and $CH_2=C(CH_2OH)CO_2R'''$,

wherein

10 R is H, F, or a C_1 - C_5 alkyl or fluoroalkyl group;

R'' is a polycyclic C_5 - C_{50} alkyl group containing at least one hydroxy group; and

R''' is a C_1 - C_{25} alkyl group; and

15 (b) a photoactive component;

(c) a solvent; and

(2) drying the coatable photoresist composition to substantially remove the solvent to form a photoresist layer on the substrate;

20 (3) imagewise exposing the photoresist layer to form imaged and non-imaged areas; and

(4) developing the exposed photoresist layer having imaged and non-imaged areas to form a relief image on the substrate.

23. The process of Claim 22, wherein R_f and R_f' of the fluorine-containing copolymer are CF_3 .

24. The process of Claim 22, wherein the developing step is performed with an aqueous alkaline developer.

25. The process of Claim 22, wherein the developing step is performed with a developer selected from the group consisting of a critical fluid, a halogenated organic solvent, and a non-halogenated organic solvent.

26. The process of Claim 25, wherein the critical fluid is carbon dioxide.

27. The process of Claim 25, wherein the halogenated solvent is a fluorocarbon compound.

28. An article of manufacture comprising a substrate coated with a photoresist composition of Claim 19.